Thermalization and Quantum Chaos in Closed Finite Electronic systems(2) Equilibrium and nonequilibrium statistical mechanics in systems showing chaos and quantum chaos, Chaos and Nonlinear Dynamics in Quantum-Mechanical and Macroscopic Systems)

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1. Introduction

It is well known that in classical mechanics an isolated system consisting of harmonic oscillators cannot be thermelized by itself. On the other hand, one consisting of anharmonic oscillators is possible to be thermelized by itself in a relatively higher energy region. It is related to the existence of *Chaos*. How about in quantum mechanics ? Quantum mechanics is linear, so there is no chaos in the sense of classical mechanics. Therefore quantum systems are never thermelized. Is it true ? Does the so-called *Quantum Chaos* play any role in thermalization of quantum systems ? This is a problem with which we are concerned ourselves in this paper.

Several authors have shown that systems consisting of a small number of interacting Fermi-particles attain thermal equilibrium due to their interaction itself [1]. In most of the cases, however, Hamiltonians are assumed to be random matrices. On the other hand, in the present paper, we employ more realistic model for Hamiltonians, whose elements are evaluated with the Gaussian-type atomic orbitals. Exact eigenstates and eigenvalues of the Hamiltonian are calculated numerically and time evolution of the system initially in some excited states is evaluated. Consequently, time evolution of an occupation number for each single-electron state, which is defined by the Hartree-Fock approximation, is obtained. The criterion for the thermalization of the system is whether the occupation numbers tend to an asymptotic distribution and is coincident with Fermi-Dirac distribution.

2. Model

The Hamiltonian of our system is written as

$$H = \sum_{i,j}\sum_{\sigma} h_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} + \frac{1}{2}\sum_{i,j,k,l}\sum_{\sigma,\sigma'} U_{ijkl} a^{\dagger}_{i\sigma} a^{\dagger}_{j\sigma'} a_{l\sigma'} a_{k\sigma} , \quad (1)$$

where i, j, k and l are stand for atomic orbital whereas σ and σ' are stand for spin. Only s-type orbital is taken into account and the integrals h_{ij} and U_{ijkl} are calculated with the Gaussian-type orbital,

$$u_i(\mathbf{r}) = (\pi/\lambda)^{-3/2} \exp(-\lambda|\mathbf{r}-\mathbf{R}_i|^2) . \quad (2)$$

The Hamiltonian (1) is diagonalized numerically and eigenenergies and eigenstates are calculated.

Single-electron sates $|\alpha>$ in the Hartree-Fock (HF) approximation are given by linear combinations $|\alpha>=\sum_{i=1}^{N} b_i^{(\alpha)}|i>$, where $|i>$ is the orbital of the i-th atom. The HF grand state and configuration-interaction (CI) states are given as $|\varphi_k>=a_{\alpha_1}^{\dagger}a_{\alpha_2}^{\dagger}\cdots\cdots|0>$ by using creation operators $a_{\alpha\sigma}^{\dagger}=\sum_{i=1}^{N} b_i^{(\alpha)}a_{i\sigma}^{\dagger}$. ($|0>$ is the vacuum.) Exact eigenstates of the Hamiltonian $|\psi_q>$ are written as linear combinations of $|\varphi_k>$'s, $|\psi_q>=\sum_k C_k^{(q)}|\varphi_k>$.

In these terms, time evolution of an arbitrary state,

$$|\Phi(t=0)>=\sum_q A_q|\psi_q> \qquad (3)$$

is given by

$$|\Phi(t)>=\sum_q A_q e^{-iE_q t}|\psi_q>, \qquad (4)$$

where E_q are eigenenergies corresponding to $|\psi_q>$. Time evolution of an occupation number for a single-electron state $|\alpha>$, $\hat{n}_{\alpha\sigma}=a_{\alpha\sigma}^{\dagger}a_{\alpha\sigma}$ is given by

$$n_{\alpha\sigma}(t)=<\Phi(t)|\hat{n}_{\alpha\sigma}|\Phi(t)>=\sum_p\sum_q A_q^{*}A_p e^{-i(E_p-E_q)t}<\psi_q|\hat{n}_{\alpha\sigma}|\psi_p> . \qquad (5)$$

If a lot of the eigenstates contribute to (5) and the sum of the off-digonal terms disappears for large times, $t=\infty$, we have asymptotic value,

$$n_{\alpha\sigma}(\infty)=\sum_q |A_q|^2<\psi_q|\hat{n}_{\alpha\sigma}|\psi_q> . \qquad (6)$$

Now we concern with the following points:

1) The sum of the off-digonal terms tends to zero ?
2) If it is the case, how fast do the occupation numbers tend to the asymptotic distribution ?
3) Is the asymptotic distribution coincident with Fermi-Dirac (F-D) distribution ?

$$n_{\alpha\sigma}(\infty)\simeq\frac{1}{1+\exp[(\varepsilon_\alpha-\mu)/T]} \qquad (7)$$

3. Numerical results

We have performed numerical calculations choosing the HF grand state and CI states as initial states.

We show results for a skewed octahedral cluster ($N=6$) illustrated in Fig.1. As a value of

the parameter λ in the basis function (2) is larger, electrons are more localized and their correlation is stronger. Therefore exact eigenstates deviate from the HF grand state and CI states as a value of λ increases. We show results for $\lambda=1$ and $\lambda=3$.

For $\lambda=1$, the H-F approximation is very good and energies of the H-F grand state and CI states are very close to exact ones as shown in Fig.2. In this case, the occupation numbers do not converge in time as shown in Fig.3.

On the other hand, for $\lambda=3$ both of energies of the H-F grand state and CI states deviate from exact eigenenergies as shown in Fig.4. In this case, the occupation numbers converge very rapidly as shown in Fig.5, where the asymptotic values (6) are plotted by the solid lines. We see that each occupation number converges in the order of 1 fsec although its oscillation remains. The asymptotic values are plotted by ○ in Fig.6 versus HF energy levels. The solid line represents a fitting with the F-D distribution function (7). As seen in this figure, the asymptotic values are approximated by the F-D distribution function very well. The energy-dependence of the temperature obtained by the above fittings is shown by ○ in Fig.7. The solid line in this figure represents temperatures in the micro-canonical statistics obtained as follows: A cumulative density of states of the system is a staircase function. We obtain a density of sates $\rho(E)$ by differentiating an approximate polynomial fitted to this staircase function. The entropy and the temperature are given by $S=\ln(\rho(E)\Delta E)$ and $1/T=\partial S/\partial E=\partial \ln\rho/\partial E$, respectively, where ΔE is an appropriate energy width. As seen in Fig.7, both kinds of temperatures are in good agreement with each other.

We have also performed similar calculations for

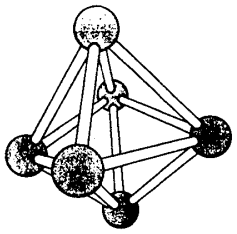

Fig.1 The skewed octahedral cluster

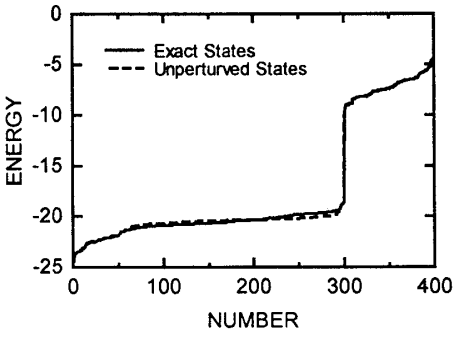

Fig.2. Exact eigenenergies and energies of the H-F grand state and CI states ($\lambda=1$)

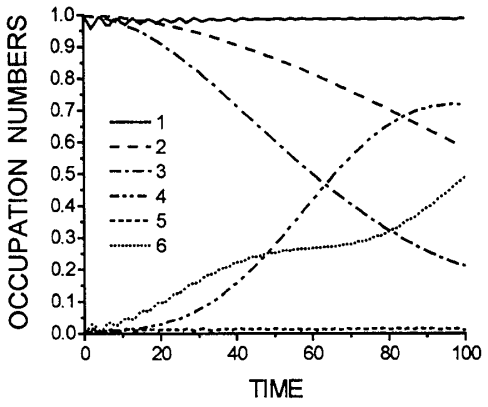

Fig.3. Time evolution of occupation numbers ($\lambda=1$)

clusters containing 8 atoms. We have found that statistical fluctuation is much more suppressed and occupation numbers converge better than in the cases of 6-atom clusters

4. Conclusion

As results of the numerical calculations, it has been found the following fact: The systems consisting of small numbers of electrons tend to thermal equilibrium due to the electron-electron interaction and distributions of occupation numbers are coincident with the F-D distribution if the electron-electron interaction is sufficiently large so that the exact eigenstates deviate from H-F grand state and CI states. Moreover, the relaxation to thermal equilibrium occurs in the order of 1 fsec.

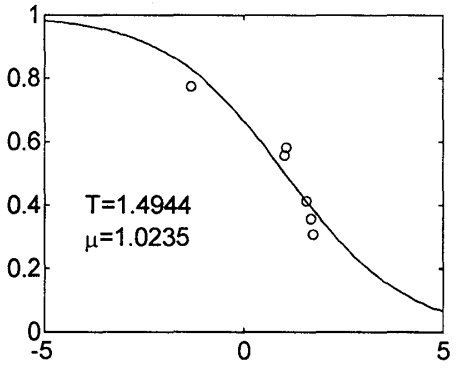

Fig.6 . The asymptotic values of occupation numbers versus single-electron energy levels.

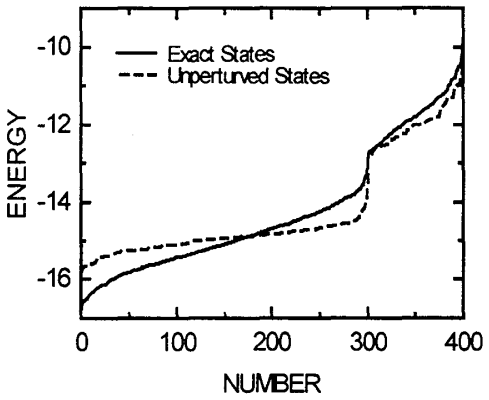

Fig.4. Exact eigenenergies and energies of H-F grand state and CI states ($\lambda = 3$)

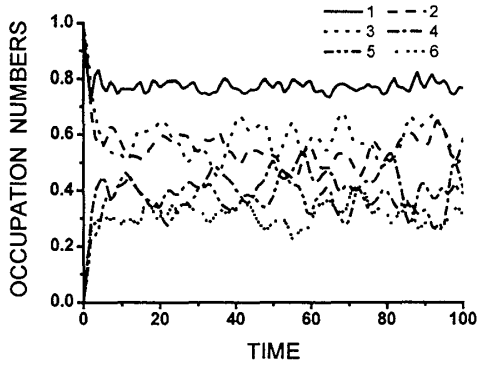

Fig.5. Time evolution of occupation number ($\lambda = 3$)

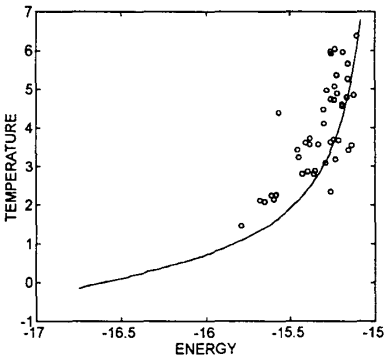

Fig.7. Energy vs. the temperature

References

[1] e.g. F.M.Izrailev; "Quantum Chaos and Thermalization for Interacting Particles", in *New Directions in Quantum Chaos : Proceedings of the International School of Physics "Enrico Fermi "*, (2000)